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SELF-DIFFUSION COEFFICIENT OF POLY(DIMETHYLSILOXANE) IN THE MELT AND IN TOLUENE AND METHYL ETHYL KETONE SOLUTIONS IN DEPENDENCE ON CONCENTRATION AND MOLECULAR WEIGHT*

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The self-diffusion coefficient of poly (dimethylsiloxane) in toluene and butanone solutions was measured in dependence on concentration and molecular weight, and also in the melt as a function of molecular weight, using NMR with time-dependent magnetic field gradient. Entanglement of poly (dimethylsiloxane) molecules in the melt commences when the molecular weight exceeds the critical value of 2500.

CONSIDERABLE and growing interest exists in translational mobility of macromolecules both in solution and in the melt. Still, the existing experimental data do not allow one to reach definite conclusions with regard to the dynamics of polymer chains in solution and in melt.

The present paper describes the work by NMR with time-dependent magnetic field gradient [1] to measure self-diffusion coefficients of several poly(dimethylsiloxane) (PDMS) fractions with molecular weight M between 5×10^2 and $7{\cdot}3\times10^5$ either in the melt or dissolved in two solvents of different thermodynamic quality: toluene (a good solvent) and methyl ethyl ketone (MEK) (a θ-solvent [2]).

The self-diffusion coefficients were measured at 313 K over the interval of polymer volume fraction $10^{-2}\leqslant\varphi\leqslant1$ with a laboratory pulsed-gradient NMR spectrometer; the proton resonance was 60 MHz and the maximum attainable value of the time-dependent magnetic field gradient was $g=50$ T/m≡[3]. PDMS fractions were prepared from commercial samples by fractional precipitation of solutions in MEK accoring to [4]. The volume fraction φ was carrulated using the value $\rho=0{\cdot}98\times10^3$ kg/m^3 for PDMS.

The self-diffusion coefficient D_s of the polymer was determined from the rate of the spin-echo attenuation plotted against the squared magnitude of the time-dependent magnetic field gradient [1, 5]. Since these plots were not purely exponential, D_s was calculated from the initial slope [6].

The concentration dependences of the self-diffusion coefficient of PDMS in toluene and in MEK are shown in Fig. 1. In both instances smooth curves without any breaks were obtained for all PDMS fractions. According to the scaling theory developed by de

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